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## INTERACTION BETWEEN STRUCTURAL ELEMENTS IN BINARY GLASSES

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Expressions for the interaction parameter as a function of macroscopic glass parameters are derived within the framework of a model taking into account the interaction between the structural elements in binary glasses. Analysis of published data established that the interaction index in alkali-silicate glasses within the temperature interval in which the temperature coefficients of expansions are constant does not depend on temperature.

An approach is proposed in [1]<sup>2</sup> making it possible to estimate the value and type of interaction between the structural elements of binary glasses on the basis of the parabolic dependence of glass density on its composition, which is optimum for describing the measurement results, and examples of applying this approach to some silicate glasses are given.

The present paper shows that the parabolic dependence is the manifestation of such properties of structural elements which make it possible to express the parameters of the specified dependence via other macroscopic characteristics of glass. First, let us refine some notions.

We define structural elements (hereafter “elements”) as compounds of the glass-constituting components that manifest and retain their individual properties as chemical compounds within a certain range of compositions with different relative contents of the components, as the interaction between the components inside the compound is significantly more perceptible than the interaction between the compounds. For instance, the structural elements of sodium silicate glasses determining the properties in the range of compositions with a molecular content of sodium oxide ranging from 0 to 20% are silica and sodium tetrasilicate, and the structural elements in potassium silicate glasses of all compositions coincide with the components.

Therefore, in the range of compositions in which the properties are formed by a certain pair of structural elements, the molar content of either of them varies from 0 to 1, as distinct from the molar content of the components. In [1] where such refinement was not made and only the notion of a “component” was used, the term “component” in a composition range in which its content varies from 0 to 1 should be understood as a “structural element.”

In accordance with the above, the dependence of the density of a binary glass on the molar content of one of its structural elements is described by the expression

$$\rho = \rho_A(1-x) + \rho_B x + \rho_{AB} x(1-x) = \rho_A + \Delta\rho x + \rho_{AB} x(1-x), \quad (1)$$

where  $\rho$  is the glass density,  $\Delta\rho = \rho_B - \rho_A$ ;  $\rho_A$  and  $\rho_B$  are the densities of the compounds representing the structural elements  $A$  and  $B$ ;  $\rho_{AB}$  is the index of the interaction between the elements;  $x$  is the molar content of the structural element  $B$  in glass of the composition  $x B - (1-x) A$ .

Expression (1) corresponds to the parabolic dependence:

$$\rho = ax^2 + bx + c; \quad (2)$$

$$\left. \begin{aligned} a &= -\rho_{AB}; \\ b &= \rho_B - \rho_A + \rho_{AB}; \\ c &= \rho_A. \end{aligned} \right\} \quad (3)$$

In this case glasses with a homogeneous structure have negative values of  $a$  and glasses prone to liquation have positive values of  $a$ . For such glasses all parameters of the dependence  $\rho(x)$  are set via the macroscopic characteristics of the components  $\rho_A$ ,  $\rho_B$ , and the molar volume ratios (hereafter “volume ratio”) of the structural elements  $k = V_A/V_B$  using the expression [1]

$$\rho = \rho_A + \frac{(\rho_B - \rho_A)x}{k(1-x) + x},$$

which can be easily transformed into Eq. (1):

$$\rho = \rho_A + \Delta\rho x + \frac{\Delta\rho(1-k)}{k-x(k-1)} x(1-x). \quad (4)$$

The first two summands in this expression represent the density variation law in the absence of interaction between the structural elements, and the last summand represents the contribution of this interaction to the dependence of density

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<sup>2</sup> Errors have been detected in the paper of V. V. Samoteikin “Interaction between ingredients of binary glasses” (*Steklo Keram.*, No. 5, 2003): the directions of arrows in Fig. 1 should be reversed; in denoting compositions (containing, for instance, components  $A$  and  $B$ ) instead of  $x B - (1-x) A$  it ought to be:  $x B (1-x) A$ .

on the composition. Comparing expressions (1) and (4) for glasses with a heterogeneous structure, we obtain

$$\rho_{AB} = \frac{\Delta\rho(1-k)}{k-x(k-1)},$$

i.e., in contrast to glasses with a homogeneous structure, the interaction index in these glasses depends on the composition. As  $k$  is a quantity of the order of 1, and the relative variation of the interaction index is not great, calculations using formula (1) can be performed using the averaged value of  $\rho_{AB}$ :

$$\langle \rho_{AB} \rangle = \Delta\rho(1-k) \int_0^1 \frac{dx}{k-x(k-1)} = -\Delta\rho \ln k. \quad (5)$$

Expression (5) for the interaction index imparts a certain sense to the volume ratio: the equality of volumes indicates the absence of interaction between the heterogeneous structural elements. In this sense they resemble ideal gas molecules, where each molecule has the same volume, regardless of the nature of gas. When the volumes differ, the type of interaction is determined by  $k$  and  $\Delta\rho$ : repulsion of structural elements ( $\rho_{AB} < 0$ ) or their attraction ( $\rho_{AB} > 0$ ).

The interaction of elements in glasses with a homogeneous structure and, accordingly, the dependence of the interaction index on macroscopic characteristics of the material will be different.

Let the structural elements  $A$  and  $B$  in a solid solution have the volumes  $V_A$  and  $V_B$  per one element. The reaction between the elements leads to their deformation and, accordingly, modifies the local density of the structural element and its dependence on the composition of the composition.

Suppose that the local density  $\rho_{A_x}$  of the element  $A$  in the variation range of the molar content  $x$  of the element  $B$  from 0 to 1 obeys the linear law (linear approximation):

$$\rho_{A_x} = \rho_A(1-x) + \rho'_A x,$$

where  $\rho_A$  and  $\rho'_A$  are the local densities of the structural element surrounded only by element  $A$  and surrounded by element  $B$ , respectively.

Similarly, for the local density  $\rho_{B_x}$  of the element  $B$  one can write

$$\rho_{B_x} = \rho_B x + \rho'_B(1-x),$$

where  $1-x$  is the molar content of the element  $A$ .

The observed density can be obtained after averaging over the local densities:

$$\rho = \rho_{A_x}(1-x) + \rho_{B_x}x = \rho_A(1-x) + \rho_B x + \rho_{AB}(1-x)x; \quad (6)$$

$$\left. \begin{aligned} \Delta\rho_A &= \rho'_A - \rho_A; \\ \Delta\rho_B &= \rho'_B - \rho_B; \\ \rho_{AB} &= \Delta\rho_A + \Delta\rho_B. \end{aligned} \right\} \quad (7)$$

Thus, expression (6) shows that successful application of the parabolic averaging method (formulas (2) and (3) from [1]) is related to a certain type of interaction between the heterogeneous components, where the interaction index is made up of the density variations of the structural elements due to their interaction with elements of a different type.

The volumes and densities of structural element are determined by the inner pressure to which they are subjected as a result of interaction with each other.

If  $P_A$  and  $P_B$  are the inner pressures in glasses consisting only structural elements  $A$  or  $B$ , the deformation of each element passing from composition  $A$  to composition  $B$  is determined by the difference  $\Delta P = P_B - P_A$ .

Let us assume that the density variation  $\Delta\rho_A$  of the structural element  $A$  under deformation is determined by the elastic properties of glasses  $A$  and the variation  $\Delta\rho_B$  by the properties of glasses  $B$ . As the interaction force in the volume on the average does not depend on the direction, this is the case of an all-around compression:

$$\left. \begin{aligned} \frac{\Delta\rho_A}{\rho_A} K_A &= \Delta P; \\ \frac{\Delta\rho_B}{\rho_B} K_B &= -\Delta P, \end{aligned} \right\} \quad (8)$$

where  $K_A$  and  $K_B$  are the moduli of all-around compression of glass compositions  $A$  and  $B$ .

It follows from expressions (8) that

$$\frac{\Delta\rho_A}{\Delta\rho_B} = -\frac{\rho_A K_B}{\rho_B K_A}. \quad (9)$$

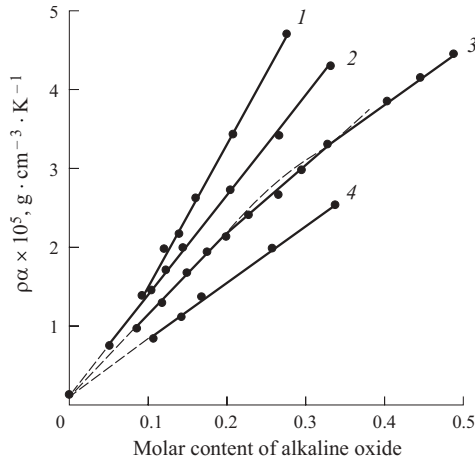
The joint solution of the system of equations (7) and (9) with respect to  $\Delta\rho_A$  and  $\Delta\rho_B$  yields

$$\left. \begin{aligned} \Delta\rho_A &= \rho_{AB} \frac{\gamma_A / \gamma_B}{(\gamma_A / \gamma_B) - 1}; \\ \Delta\rho_B &= \rho_{AB} \frac{1}{1 - (\gamma_A / \gamma_B)}. \end{aligned} \right\} \quad (10)$$

where  $\gamma_A = \rho_A / K_A$ ;  $\gamma_B = \rho_B / K_B$ .

Thus, expressions (10) make it possible to relate the local density variation of each structural element with the elastic constants of glasses of the respective compositions and estimate these variations.

For instance, all indications of a heterogeneous structure are identified for the  $\text{Na}_2\text{O} - \text{SiO}_2$  system in the composition range  $0 < x < 0.2$ , in particular the negative value of the interaction index  $\rho_{AB}$  obtained as a result of parabolic averaging of the dependence of density on composition [1], when  $\text{SiO}_2$  and  $0.2\text{Na}_2\text{O} - 0.8\text{SiO}_2$ , respectively, are taken as structural elements  $A$  and  $B$ . If the glasses of this system formed a homogeneous structure consisting of structural elements  $\text{SiO}_2$  and  $\text{Na}_2\text{O}$ , their interaction index would be positive and equal to  $0.88 \text{ g/cm}^3$ . If a homogeneous structure in the com-



**Fig. 1.** Temperature expansion of different alkali-silicate glasses depending on compositions: 1)  $\text{Rb}_2\text{O}-\text{SiO}_2$  (20–400°C), Yu. A. Shmidt and Z. D. Alekseeva [2]; 2)  $\text{K}_2\text{O}-\text{SiO}_2$  (20–400°C), Yu. A. Shmidt and Z. D. Alekseeva [2]; 3)  $\text{Na}_2\text{O}-\text{SiO}_2$  (0–130°C), W. E. C. Turner and T. Winks [2]; 4)  $\text{Li}_2\text{O}-\text{SiO}_2$ , V. V. Vargin, M. V. Zasolotskaya, N. E. Kind, et al. [3].

position range  $0 < x < 0.2$  consisted of the specified elements  $A$  and  $B$ , then  $\rho_{AB} = 0.88 \times 0.2^2 = 0.035 \text{ g/cm}^3$ .

In this case, variations in local densities  $\Delta\rho_A$  and  $\Delta\rho_B$  calculated on the basis of formulas (10) would be equal to  $\Delta\rho_A = -0.283 \text{ g/cm}^3$  and  $\Delta\rho_B = 0.318 \text{ g/cm}^3$ . The values  $K_A = 3.6 \times 10^{10} \text{ Pa}$  and  $K_B = 3.55 \times 10^{10} \text{ Pa}$  assumed here are taken from the reference book [2]. This means that incorporation of the structural element  $B$  into the structure of  $A$  loosens the latter, while the element  $B$  becomes condensed. Since adjacent heterogeneous structural elements experience perceptible deformation, it is preferable to have a heterogeneous structure in which stresses arise at the boundaries between the phases formed by the structural elements.

Let us apply the specified approach to studying the dependence of thermal expansion parameters on the composition.

Let us analyze the temperature interval in which the temperature coefficients of linear  $\alpha$  and volume  $\beta$  expansion can be regarded as constant. Since  $\beta = \frac{1}{V} \frac{dV}{dt}$  and  $\frac{dV}{V} = -\frac{d\rho}{\rho}$ , then

$$\rho\beta = -\frac{d\rho}{dt}, \quad (11)$$

where  $t$  is the temperature.

Differentiating expression (2) with respect to temperature and taking into account formulas (3) and (11), we obtain

$$\rho\beta = c' + b'x + a'x^2; \quad (12)$$

$$\left. \begin{aligned} c' &= \frac{d\rho_A}{dt} = \rho_A\beta_A; \\ b' &= -\frac{db}{dt} = \rho_B\beta_B - \rho_A\beta_A - a'; \\ a' &= -\frac{da}{dt}. \end{aligned} \right\} \quad (13)$$

It follows from Eq. (12) that the product  $\rho\beta$  (or  $\rho\alpha$ , since the temperature coefficients of linear and volume expansion are proportional) has to obey a parabolic dependence on the molar content of the structural element.

Figure 1 represents these dependences for some alkali-silicate glasses of homogeneous and heterogeneous compositions. Dilatometric data are taken from the authors who also supplied data on the density of the samples considered. All density values are determined at room temperature. For glasses with a homogeneous structure the dependence  $\alpha\rho$  on  $x$  is linear with a constant value of coefficients  $b'$  in the entire composition range considered, whereas the curves for glasses with a heterogeneous structure have several linear segments. It can be inferred that in the temperature interval considered  $a' = 0$  and the interaction index does not change with changing temperature. Then  $b' = \rho_B\alpha_B - \rho_A\alpha_A$  and together with expressions (13) it describes the dilatometric properties of alkali-silicate glasses in a temperature interval up to 400°C. The emergence of breaks on this curve in the case of sodium-silicate glasses is related to a change in the structural elements passing from certain compositions to others.

Thus, representing dilatometric measurements in the form of dependence  $\rho\alpha(x)$  makes it possible to identify the boundaries of the compositions in which glass properties are determined by different structural elements.

## REFERENCES

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